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Review

Use of organotin halides as catalytic precursors in dehydration processes *

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Abstract

Organotin halides of the type $R_{4-n}SnX_n$ (R = organic group, X = halide, $n = 2$ or 3) have been shown to be useful catalytic precursors for dehydration processes. Particularly useful is $BuSnCl_3$, an inexpensive, easily-handled, and effective compound; $BuSnCl_3$ promotes (i) etherification of allylic alcohols and 1,*n*-acyclic diols, (ii) cyclization of 2,5-hexanedione, (iii) dehydration of cyclic diols, and (iv) acetalizations (and transacetalizations) of R'CHO, using diols and polyols. For processes i–iii, $RO(Bu)SnCl_2$ are probable intermediates, whereas in iv, activation of R'CHO by $BuSnCl_3$ is considered important.

Introduction

Organotin compounds are extensively used as homogeneous catalysts, as in esterifications and transesterifications, in formation of organosilicon binders, in dehydrogenation and isomerization reactions [1].

Triorganotin alkoxides (R_3SnOR') have been suggested to be the effective reagents in transesterifications [2] and other reactions [3]. Even more reactive species are organotin halide alkoxides, $R_{3-n}(R'O)SnX_n$ ($n = 1$ or 2) [4–6]: the enhanced reactivity is due to the electron-withdrawing halide groups rendering the tin more positive [6]. Such alkoxides can readily be formed as shown in eq. 1 [7].

$$R'{-}OH + R_{4-n}SnX_n = R_{4-n}(R'O)SnX_{n-1} + H{-}X \qquad (1)$$

$(n = 1\text{–}3)$

This short review is concerned with dehydration reactions of hydroxy or enolic species [5,8,9] and with acetalization and transacetalization of R'CHO using diols and polyols [10–12], mediated by organotin halides, in particular by $BuSnCl_3$.

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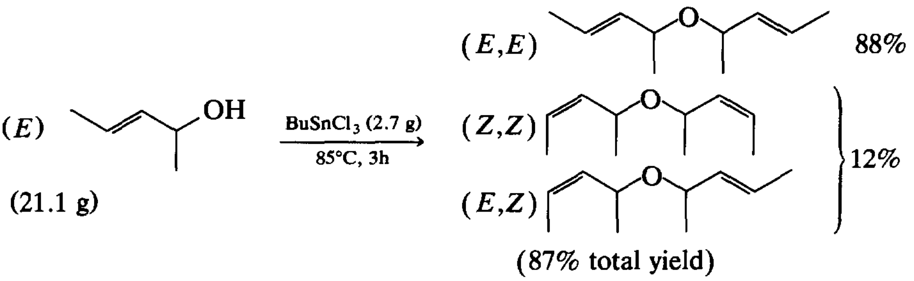
* Dedicated to Professor Alwyn G. Davies in recognition of his important and distinguished contributions to organometallic chemistry.

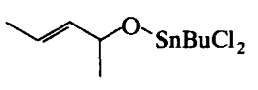
Formation of diallyl ethers from allylic alcohols

Butyltin trichloride has been found to dehydrate various compounds $RCR^1{=}CH\text{-}CH(OH)R^2$, *e.g.* (*E*)/(*Z*)-$CH_3CH{=}CHCH_2OH$, (*E*)-$CH_3CH{=}CHCH(OH)CH_3$, $(CH_3)_2C{=}CHCH_2OH$ [9] and $CH_3CH{=}CH\text{-}CH(OH)\text{-}CH_2CH{=}CH_2$ as well as $CH_3CH{=}CH\text{-}CH(OH)\text{-}CH(R)\text{-}CH{=}CH_2$ ($R = CH_3$ or $CH_2CH_2CH_3$) [5]. However, $CH_2{=}CHCH(OH)CH_3$ is unreactive, as are primary, secondary, and tertiary alkanols. At ratios of [alkenol]/[$BuSnCl_3$] between 6 and 25, and at temperatures between 20 and 145°C, reactive alkenols are converted to mixtures of isomeric ethers in good yields (80–90%). As an example, Scheme 1 shows the dehydration products of (*E*)-3-penten-2-ol. Three isomeric species are formed: the major product (88%) is the unrearranged ether with (*E*,*E*)-geometries, whereas the other two (*Z*,*Z*) and (*E*,*Z*) (total, 12%) contain rearranged allylic moieties, due to hydroxy-1,3-sigmatropic shifts [13].

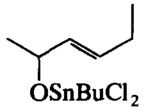


Scheme 1. Catalytic dehydration of (*E*)-3-penten-2-ol mediated by $BuSnCl_3$.

In all cases [5], the major product (75–90%) is the ether containing unrearranged allylic groups. The isomeric composition in the etherification of $CH_3CH{=}CH\text{-}CH(OH)CH_2CH{=}CH_2$, in the presence of $BuSnCl_3$ is the same as that obtained in the thermal reaction of $CH_3CH{=}CHCHO$ and $CH_2{=}CHCH_2SnBuCl_2$ [14]. This confirms the hypothesis [5] that organoalkoxytin dichlorides of the types shown



(*E*-unrearranged alkoxide)



(*Z*-rearranged alkoxide)

are intermediates in both catalytic and allylstannation processes.

Formation of cyclic ethers from diols

Several organotin halides have been tested as catalysts of the cyclization of diols to cyclic ethers [5,9] (eq. 2).

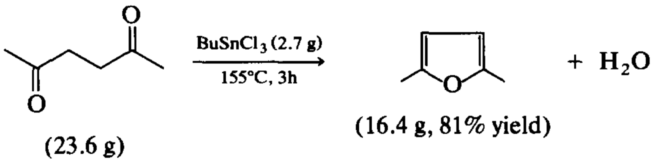
$$HO\text{-}(CH_2)_n\text{-}OH \xrightarrow[180\text{–}250^\circ C]{\text{Organotin halide}} \left(CH_2)_n\,O\right. \qquad (2)$$

(n = 4, 5, or 6)

The diol conversion diol rate (g h^{-1}) has been used as a measure of the catalytic efficiency of the organotin halide. At constant molar ratio [diol]/[Sn] of 20, the relative activities are as shown: $MeSnCl_3 \geqslant PhSnCl_3 > SnCl_4 > BuSnCl_3 \gg Me_2SnCl_2 > Bu_2SnCl_2 \gg [Bu_2SnCl]_2O$

Tributyltin trichloride is fairly active: its 1,5-pentanediol conversion rate to tetrahydropyran is 26.1 g h^{-1} at 190–210°C (compared to 41.6 for $MeSnCl_3$ at 200–215°C and 8.4 for Me_2SnCl_2 at 235–245°C). However, compared to $MeSnCl_3$, $PhSnCl_3$, and $SnCl_4$, butyltin trichloride is easy to handle, is not expensive, and is sufficiently reactive in these reactions. Using $BuSnCl_3$ and suitable diols, the following cyclic ethers have been obtained: tetrahydrofuran, 2-methyltetrahydrofuran, 2,5-dimethyltetrahydrofuran, 2,5-dihydrofuran, tetrahydropyran, 2-methyltetrahydropyran, 1,4-dioxane, 2,4-diallyltetrahydropyran. Triols can also be made: 3-hydroxy-tetrahydrofuran and 3-hydroxymethyltetrahydropyran were prepared in 92 and 70% yields, respectively, from 1,3,4-trihydroxypropane and 1,5,6-trihydroxyhexane [9]. In all cases, using $BuSnCl_3$ has some advantages over methods previously reported [15–18] (*cf.* Table 1).

A related preparation is that of 2,5-dimethylfuran from acetonylacetone (eq. 3).

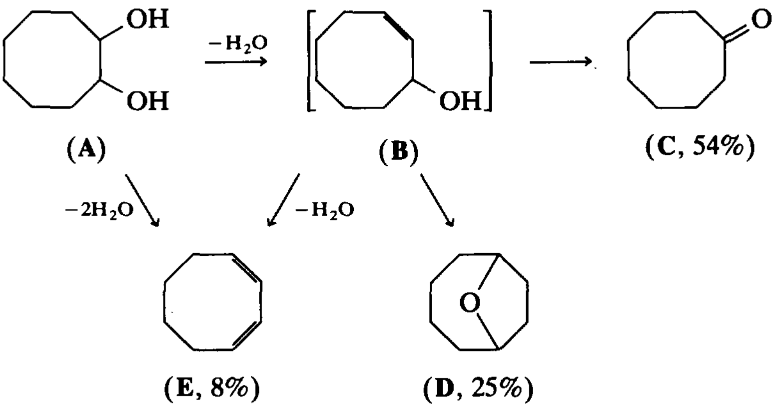


(3)

This is an example of a cyclodehydration occurring via the enolic form of a ketone. Sulphuric acid has been previously reported to effect this reaction [19].

Dehydrations of alicyclic diols

Alicyclic diols such as 1,3-cyclopentane-, 1,4-cyclohexane-, and 1,2-cyclooctanediols, when heated to 180–235°C in the presence of $BuSnCl_3$ ([diol]/[$BuSnCl_3$] in the range 20–40) give rise to mixtures of dehydrated products [9]. An example is given in Scheme 2, which shows the conversion of 1,2-cyclooctanediol (**A**) to a mixture of cyclooctanone (**C**), 1,4-epoxycyclooctane (**D**), together with a small



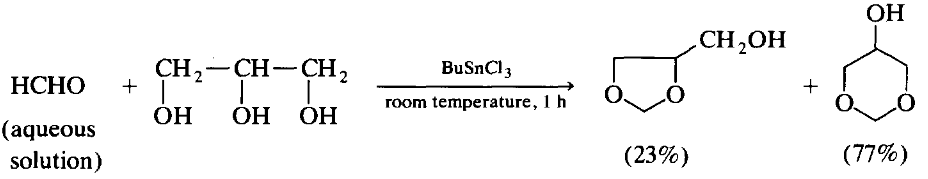
Scheme 2. Dehydration of 1,2-cyclooctanediol (36.1 g) mediated by $BuSnCl_3$ at 180–215°C, 1 h (recovered mixture 27 g, 86%).

amount of 1,3-cyclooctadiene (**E**). The total conversion of the cyclic diol is 86%. The primary formation of 2-cyclooctene-1-ol (**B**) by 2-hydroxy-elimination has been suggested. The two main products, **C** (54%) and **D** (25%), may arise from an intramolecular rearrangement of **B**. It is noteworthy that in the dehydration of 1,3-cyclopentane- and 1,4-cyclohexane-diols, the processes are simply 2-hydrohydroxy-eliminations.

Acetalizations using diols and triols

Butyltin trichloride, thanks to its ability to act both as an acid and as a dehydrating agent, has been used for acetalizations using diols and polyols. There are several advantages in using $BuSnCl_3$ [10–12] compared to other methods [20].

Many diols [10,12] and triols [11], such as 1,2,3-propanetriol and 1,2,4-butanetriol, form acetals with various aldehydes in the presence of $BuSnCl_3$. Reactions occur under mild conditions, with short reaction times and in the absence of solvent. Work-up is very easy and pure acetals are isolated in high yields (80–98%). It is remarkable that acetalizations with $BuSnCl_3$ can also be performed in the presence of water: even aqueous solutions of aldehydes can be used, as the following example indicates (eq. 4).



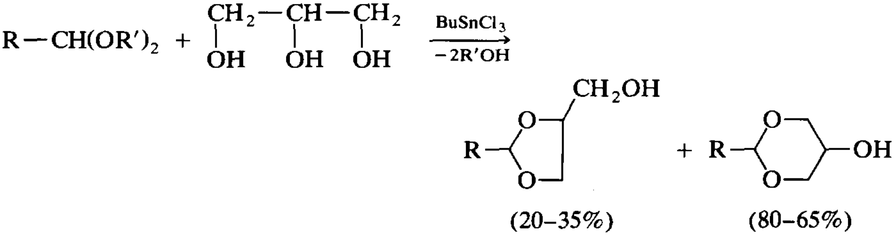
(4)

This finding is very significant since the removal of water is generally the main concern in acetalizations; the removal of water by azeotropic distillation or by chemical methods [21], is thought necessary to drive the equilibrium over to the side of acetal formation.

Transacetalizations

Transacetalizations of aldehyde dialkyl acetals, $RCH(OR')_2$, with diols and polyols can also be carried out using $BuSnCl_3$ as the catalyst precursor [11,12]. As with acetalizations, reactions occur under mild conditions, with short reaction times and in the absence of solvent. Again, the presence of water can be tolerated.

As in acetalizations, reactions of 1,2,3-propanetriol (glycerol) with aldehyde dimethyl- or diethyl-acetals provide mixtures of five-membered (1,3-dioxolanes) and six-membered (1,3-dioxanes) cyclic acetals; the latter are the major products (eq. 5).

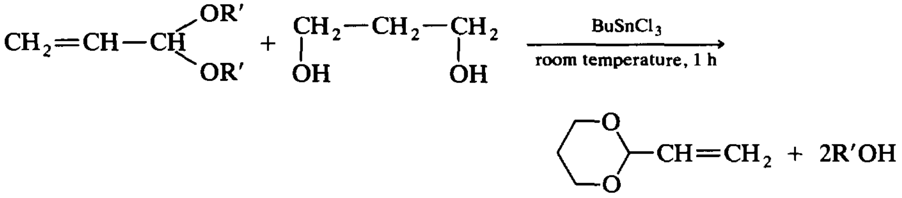


(5)

(R = alkyl, R' = CH_3 or C_2H_5)

When halomethyl acetals are employed, the 1,3-dioxolanes become the major products, as expected from the presence of electron-withdrawing groups [22]. Six-membered cyclic acetals are the major products in the transacetalizations by 1,2,4-butanetriol of $RCH(OR')_2$ ($R = CH_3$, C_2H_5, CH_2Cl, CH_2Br, CH_3OCH_2-CH_2, or CH_2=CH [11]).

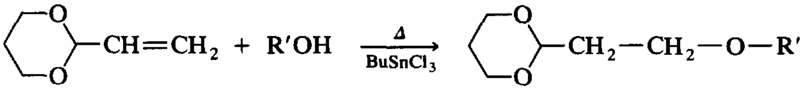
2-Vinyl-1,3-dioxane, previously prepared by various methods [23,24], may be readily synthesized by the present procedure with yields between 70 and 95%. The yield is strongly dependent on the reaction procedure and the temperature used to remove the methanol or the ethanol, co-products of the transacetalization process (eq. 6).



(6)

($R' = CH_3$ or C_2H_5)

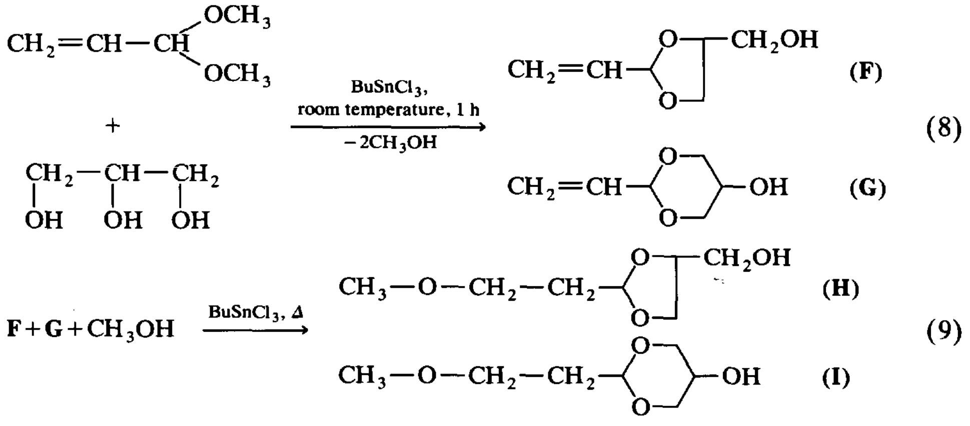
If the reaction mixture is heated after leaving for 1 h at room temperature, the following secondary reaction occurs (eq. 7).



(7)

The alcohol co-product adds to the activated carbon–carbon double bond [25] with the formation of 2-(2-alkoxyethyl)-1,3-dioxane.

Reactions of both 1,2,3-propane- and 1,2,4-butane-triols with acrolein dialkyl acetals occur in the same way, as depicted in Scheme 3. In such cases, the products depend on the experimental conditions. Cyclic acetals **F** and **G** can be isolated by simply removing the alcohol co-product under mild work-up (eq. 8). However, if the system is heated, reaction 9 occurs giving acetals **H** and **I**.



Scheme 3. Reactions involving acrolein dimethyl acetal and glycerol.

Table 1

Comparison of the "BuSnCl$_3$" and other processes

Type of reactions	Conversion of	BuSnCl$_3$ procedure [a]		Other procedure		
		Yield %	Ref.	Catalyst	Yield (%)	Ref.
Etherification of allyl alcohols	3-Methyl-2-buten-1-ol to ethers I, II, and III [b]	90	9	$BF_3 \cdot OEt_2$	36 [c]	32
Conversion of diols and triols to cyclic ethers	$(HOCH_2CH_2)_2O$ to 1,4-dioxane	62	9	Nafion-H [d]	50	33
	$HOCH_2(CH_2)_2CH_2OH$ to tetrahydrofuran	94	5	Nafion-H [d]	91	33
	$HOCH_2(CH_2)_2CH(OH)CH_3$ to 2-methyl-tetrahydrofuran	96	5	Nafion-H [d]	90	33
	$HOCH_2(CH_2)_3CH_2OH$ to tetrahydropyran	98	5	Nafion-H [d]	86	33
	(*Z*)-2-Buten-1,4-diol to 2,5-dihydrofuran	88	9	I_2	40	34
				TPP–t-BHC [e]	61	35
	(*Z*)-1,2-Bis(hydroxymethyl)-cyclohexane to (*Z*)-8-oxa-bicyclo-4,3,0-nonane	92	9	$(CH_3)_2O$	66	36
				H_2SO_4	24	34
				TPP–t-BHC [e]	99	35
				DTPP–CH_2Cl_2 [f]	76	37
				DTPP–toluene [g]	95	38
	1,2,4-Butanetriol to 3-hydroxy-tetrahydrofuran	92	9	*p*-TSA [h]	81–88	15,16
				DEC [i]	88	17
	1,2,6-Hexanetriol to 2-hydroxymethyl-tetrahydropyran	65	9	EC [j]	62	17

[a] Data are given for [alcohol]/[BuSnCl$_3$] = 20. [b] I = $[(CH_3)_2C{=}CHCH_2{-}]_2O$, (75%); II = $(CH_3)C{=}CHCH_2O{-}C(CH_3)_2CH{=}CH_2$, (16%); III = $[CH_2{=}CHC(CH_3)_2{-}]_2O$, (9%). [c] The mixture contains 4% of ether I and 32% of ether II. [d] Nafion-H is a trade name of the DuPont Co. for a perfluorinated sulphonic acid resin. [e] TPP–t-BHC, triphenylphosphine and tert-butylhypochlorite. [f] DTPP, diethoxytriphenylphosphorane in CH_2Cl_2. [g] DTPP in toluene. [h] *p*-TSA, *p*-toluenesulphonic acid. [i] DEC, diethyl carbonate. Stoichiometric reaction of the DEC ester. [j] EC, ethylene carbonate. Stoichiometric reaction of the EC ester.

Some comments about catalytic processes mediated by organotin halides

A number of tin compounds are marketed today as esterification and transesterification catalysts in industrial processes [26], since they have advantages over traditional strong proton acid catalysts such as *p*-toluenesulphonic acid. Recently, monoalkyltin compounds have also been shown to be effective transesterification catalysts [27]; studies have been carried out on the transesterification reaction between butyl propionate and an excess of methanol in the presence of 0.2 mol% of various monoalkyltin compounds [28]. In addition, transesterification of carboxylic esters and the esterification of carboxylic acids have been effected under mild conditions using 1,3-disubstituted tetraalkyldistannoxanes as catalysts [29,30]. Nevertheless, it seems that transesterification and esterification processes are better catalysed by basic organotin derivatives, whereas etherification processes need acidic organotin substrates. We recall that the catalytic activity of organotins in the conversion of 1,5-pentanediol to tetrahydropyran decreases on passing from acidic species such as $RSnCl_3$ to more basic species such as $[Bu_2SnCl]_2O$ [5]. The same trend is observed in the etherification processes of allyl alcohols [31].

We have shown that the use of $BuSnCl_3$ has some advantages over other acidic organotin species in promoting some dehydration processes. This efficiency is also observed when other catalysts are compared. Table 1 provides a comparison between the efficiency of our "$BuSnCl_3$" process and those using other catalysts.

Acetalization and transacetalization processes performed with $BuSnCl_3$ at room temperature and short reaction times, show some advantages over procedures using Amberlite IR-20 at 93°C [39], KU-2-8-ion exchange resin [40], HCl [41], *p*-toluenesulphonic acid [24], calcium sulphate, molecular sieves, and removal of water by dehydrating agents or azeotropic distillation.

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